Analysis of ^{14}C-bearing compounds released by the corrosion of irradiated steel using accelerator mass spectrometry

B. Z. Cvetković[a], G. Salazar[b], D. Kunz[a], S. Szidat[b], E. Wieland[a]

[a]Paul Scherrer Institut, Laboratory for Waste Management, 5232 Villigen PSI, Switzerland. E-mail: benjamin.cvetkovic@psi.ch

[b]University of Bern, Department of Chemistry and Biochemistry & Oeschger Centre for Climate Change Research, 3012 Bern, Switzerland

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Abstract

The combination of ion chromatography (IC) with accelerator mass spectrometry (AMS) was developed to determine the speciation of ^{14}C-(radiocarbon) bearing organic compounds in the femto to pico molar concentration range. The development of this compound-specific radiocarbon analysis (CSRA) of carboxylic acids is reported and the application of the method on a leaching solution from neutron-irradiated steel is demonstrated. Background and dynamic range of the AMS-based method were quantified. Using ^{14}C-labelled standards, the measurements demonstrate the repeatability of the analytical method and the reproducible recovery for the main target carboxylic acids (i.e., acetate, formate, malonate, and oxalate). The detection limit was determined to be in the mid fmol ^{14}C/L level while the dynamic range of the analytical method covers three orders of magnitude from the low fmol to mid pmol ^{14}C/L level. Cross contamination was found to be negligible during IC fractionation and was accounted for during eluate processing and ^{14}C detection by AMS. The ^{14}C-bearing carboxylates released from an irradiated steel nut into an alkaline leaching solution were analysed using the CSRA-based analytical method with the aim to check the applicability of the approach and develop appropriate sample preparation. The concentrations of ^{14}C-bearing formate and acetate, the main organic corrosion products, were at low pmol ^{14}C/L level for convenient dimensions of the alkaline leaching experiment which demonstrates that compound-specific ^{14}C AMS is an extremly sensitive analytical method for analysing ^{14}C-bearing compounds. The content of total organic ^{14}C in solution (TO^{14}C) determined by direct meassurement of an aliquot of the leaching solution agrees well with the sum of the ^{14}C concentrations of the individual carboxylates within the uncertainty of the data. The TO^{14}C content further is in good agreement with the calculated value using the corrosion rate determined from ^{60}Co release and the ^{14}C inventory of the irradiated steel specimen.

Introduction

In several countries worldwide the concept of safe disposal of radioactive waste in deep geological repositories is currently developed[1]. Radiocarbon was identified as a dose-determining radionuclide in radioactive waste and a key radionuclide in safety assessments (SA) for nuclear waste repositories due to its long half-life (5730 a), its potential presence as either dissolved or gaseous species, and due to the high mobility of dissolved ^{14}C-bearing organic compounds in the host rock[2,3]. In current SA, it is assumed that ^{14}C contributes to the dose in the inorganic chemical form, i.e. ^{14}C-bicarbonate and ^{14}C-carbonate, in the organic form, i.e. as ^{14}C-bearing organic compounds, and in the gaseous chemical form, i.e. ^{14}C-bearing hydrocarbons[2]. While the total ^{14}C inventory of a repository is mostly understood, the chemical nature of the ^{14}C-bearing compounds is only poorly known. However such knowledge is essential with a view to assigning possible release paths from the repository near-field into the host rock, the groundwater and the biosphere. Identification and quantification of ^{14}C-bearing organic compounds is of particular importance as these compounds are only weakly retarded in the engineered barrier of a repository and the host rock, and therefore may substantially contribute to the dose release with time.

Compilations of the radionuclide inventories of radioactive waste in Switzerland show that the ^{14}C inventory of a cement-based repository for low- and intermediate-level waste (L/ILW) is mainly associated with irradiated steel (~ 75 %). ^{14}C containing steel is primarily produced as a result of the activation of ^{14}N associated with nitrogen impurities contained in nuclear fuel components and metal components of the core structural materials by thermal neutrons according to the reaction ^{14}N(n,p)^{14}C[4,5]. Slow corrosion of irradiated steel in the anoxic alkaline conditions of a cement-based repository may occur and release ^{14}C into the repository near-field. Previous corrosion studies with powders of non-irradiated carbon steel showed the formation of different classes of organic compounds such as short-chain hydrocarbons with a carbon chain length between C1 and C5[6–8], low-molecular-weight carboxylic acids (C1-C3), and alcohols and aldehydes (C1-C3)[8–11]. Nevertheless, it is presently not clear whether or not the same carbon species could also form during the anoxic corrosion of irradiated steel in alkaline media, because the chemical form of ^{12}C in non-irradiated carbon steel (mainly Fe_3C) and ^{14}C in irradiated stainless steel (presumably ^{14}C bound in interstices of the lattice structure of the steel) might be different[12].

To date, there is no analytical approach available that allows a direct analysis of the speciation of ^{14}C-bearing organic corrosion products at the very low concentration levels required for corrosion studies with irradiated steel.

The laboratory-scale set-up employed in the present work was limited to a sample size of 1 – 2 g of irradiated steel due to the high dose rate of ~30 mSv/h/g of steel (mostly ^{60}Co)[13]. The ^{14}C concentration however is low (~18 kBq ^{14}C per g steel)[13] and the release rate of ^{14}C was estimated to range between a few femto- to a few picomoles ^{14}C per litre

and day as a consequence of the very slow corrosion of steel (a few nm/year)[14,15] in alkaline solution.
The aqueous ^{14}C concentration is further reduced when chromatographic fractionation is applied for the analysis of single ^{14}C-containing species due to dilution with the eluent. For the above reasons, identification and quantification of ^{14}C-bearing compounds requires an extremely sensitive analytical method in the corrosion studies with irradiated steel. The most suitable analytical technique to achieve the required sensitivity is compound-specific radiocarbon (CSRA) accelerator mass spectrometry (AMS). AMS is commonly known and used in radiocarbon dating[16,17]. This technique allows the detection of very low ^{14}C contents by efficient separation of isobaric interferences and ultra-sensitive direct detection of the rare isotope[18]. The abundant isotopes ^{12}C and ^{13}C are also measured to express the results in ratio. Note that AMS does not depend on the disintegration of the radionuclides, in contrast to radio-analytical techniques for ^{14}C detection, such as liquid scintillation counting. Therefore, AMS has a much lower detection limit. Furthermore, the method requires only small sample volumes and takes less time for a single analysis[18,19].
In this study, the development of an analytical method is reported, which allows direct measurement of the ^{14}C speciation at very low ^{14}C concentrations on the basis of CSRA AMS. The method is based on the combination of high performance ion exchange chromatography (HPIEC) for the fractionation of the ^{14}C-bearing carboxylic acids and ^{14}C quantification by AMS. Application of the method is demonstrated by identifying and quantifying the ^{14}C-bearing carboxylates present in a leaching solution containing a specimen of irradiated steel with a weight of 1 g.

Experimental

Sample preparation

Chemicals and solutions. Throughout this study, the solutions were prepared by using Fluka or Merck analytical-grade ("pro analysis") chemicals. Ultrapure water (18.2 MΩ · cm) was generated by a Milli-Q Gradient A10 purification system (Millipore, Bedford, MA, USA), which was used for the preparation of solutions and standards. Boiled ultrapure water was prepared by boiling ultrapure water for about 2 hours under continuous nitrogen (N_2) purge to remove dissolved oxygen (O_2) and carbon dioxide (CO_2). The container with the ultrapure water was sealed and introduced into a glovebox with a N_2 atmosphere prior to use. In addition for certain background experiments deionized water (LC-MS grade, Merck, Germany) was used.

In this study, an artificial cement pore water (ACW) was used with a chemical composition corresponding to a solution in equilibrium with cement paste degraded to the stage II of cement degradation[20]. The solution was prepared as follows: CaO was prepared by decomposing $CaCO_3$ at 1000°C until a constant weight was achieved. 2 g of CaO were

mixed with 1 L boiled ultrapure water and equilibrated on an end-over-end rotor for at least two days in the glovebox with N_2 atmosphere. After equilibration, the suspension was filtered using a 100 nm polyethersulfone membrane filter (Criticap-MTM, Gelman Science, USA). Thus, the solution was saturated with respect to portlandite and had a pH of 12.5.

The following ^{14}C-labelled tracers were used for the recovery and cross contamination tests: sodium [1,2-^{14}C]acetate (radiochemical purity > 97 %, PerkinElmer, Boston, USA), sodium [^{14}C]formate (radiochemical purity 99%, ARC, St. Louis, USA), [2-^{14}C]malonic acid (radiochemical purity 99 %, ARC, St. Louis, USA), [U-^{14}C]oxalic acid (radiochemical purity 99 %, ARC, St. Louis, USA).

Standards. Sodium acetate (AA), sodium formate (FA), malonic acid (MA), and oxalic acid (OA), respectively, were dissolved in 50 mL ultrapure water for the preparation of 10 mM carboxylic acid stock solutions. A multi-component solution (10 mL) containing sodium acetate, sodium formate, malonic acid and oxalic acid at concentrations 500, 500, 200 and 200 µM, respectively, was prepared by diluting appropriate aliquots of the individual stock solution with ultrapure water. Calibration standards were prepared from this multi-component solution for the HPIEC analysis in the concentrations of 0, 3.5, 6.5, 40, 130, 250, 500(AA), 0, 3.5, 6.5, 40, 130, 250, 500 (FA), 0, 1.5, 3, 15, 50, 100, 200 (MA), 0, 1.5, 3, 15, 50, 100, 200µM (OA), respectively. All solutions were stored at 4 °C in the refrigerator.

Sample pre-treatment. Prior to fractionation, the aliquots from the leaching solution and all standards prepared in ACW, were pre-treated using an OnGuard® II Ba/Ag/H cartridge (Dionex/Thermo Fisher, Sunnyvale, CA, USA). The pre-treatment adjusted the pH to a near-neutral value and removed interfering ions which improved the reproducibility of the fractionation process. In addition, inorganic ^{14}C (i.e. $^{14}CO_3^{2-}$ at pH 12.5) was quantitatively removed from solution. The cartridges were conditioned with 10 mL ultrapure water prior to use. Approximately 4.75 mL of each sample solution was pushed through the cartridge. The first 4 mL were discarded and the last 0.75 mL of the eluted solution was collected for analysis. All samples were stored at 4 °C and analysed within 24 h at the latest. Efficiency of the cartridge treatment was determined with standard solutions of carboxylic acids which were analysed with and without cartridge treatment with HPIEC with conductivity detection. Recoveries were found to be 99 ± 2 % for all four target carboxylic acids.

Leaching experiment

An irradiated steel nut segment (1 g) was immersed in 29.3 mL ACW solution in a polypropylene container and leached over a period of 1046 days (i.e., 2.87 years) in a hotcell under atmospheric (oxic) conditions. Characterisation of the used steel nut was reported in detail elsewhere[13]. It had a high dose rate (in the range of several tenth of

mSv/h) due to the presence of activated metals (e.g. ^{60}Co), but its ^{14}C content was low (7.71 ± 1.08 nmol ^{14}C/g)[13]. The steel nut segment was removed from solution prior to the determination of ^{60}Co by gamma spectrometry and sampling of aliquots of the leaching solution for AMS measurements. The aliquots were used to determine the individual ^{14}C-bearing carboxylates and for a direct AMS measurement (without fractionation) of the total organic radiocarbon.

High performance ion exchange chromatography (HPIEC)

The ICS-5000 ion chromatography (IC) system (Dionex/Thermo Fisher, Sunnyvale, CA, USA) used in this study has an EG-40 eluent generator and was connected to an AS-50 auto sampler and a CD-25 conductivity detector (CD). The carboxylic acids were separated by using a 250 mm × 2 mm i.d. IonPac AS11-HC column in combination with the corresponding guard column (Dionex/Thermo Fisher, Sunnyvale, CA, USA). A 2 mm ASRS-Ultra suppressor operated in the external water mode is installed before the conductivity cell. The analytical column was operated at 30 °C (column thermostat TCC-100). The optimized mobile phase was aqueous KOH, produced by the eluent generator (EG-40) and the following KOH concentration gradient was applied: 0-15 min: isocratic at 1.0 mM; 15 - 35 min: gradient from 1 - 30 mM; 35 - 40 min: isocratic at 30 mM; 40 - 41 min: gradient from 30 - 1 mM; 41 - 46 min: isocratic at 1 mM. The samples were injected via an injection loop of 14 µL and eluted using a flow rate of 0.25 mL/min. The retention times determined for the carboxylic acids were as follows: 8.7 min AA, 10.5 min FA, 28.9 min MA, 30.8 min OA.

For fractionation of the carboxylic acids, a fraction collector (Foxy Jr. Fraction collector, Teledyne Isco, Lincoln, NE, USA) was connected to the conductivity detector of the chromatographic system. Fractions were collected based on their retention times which were checked before each experiment using non-labelled standards. The fractions were directly collected into pre-cleaned vials made of polypropylene (PP).

The HPIEC system was purged after each sample injection with ultrapure water by using a modified program (0 - 1 min: isocratic at 1.0 mM; 1 - 2.5 min: gradient from 1 - 30 mM; 2.5 - 4.5 min: isocratic at 30 mM; 4.5 - 5.0 min: gradient from 30 - 1 mM; 5 - 11.5 min: isocratic at 1 mM).

Gamma spectrometry

The ^{60}Co activity of the leaching solution was determined at 1173.2 and 1332.5 keV with gamma spectrometry (Ortec-Ametek GEM-25185, Berwyn, PA, USA). To this end, the irradiated steel nut was removed from the leaching solution. The container with the leaching solution was weighed and placed in the gamma spectrometer.

Accelerator mass spectrometry (AMS)

^{14}C analysis of the samples was performed on a 200 kV MICADAS (MIni CArbon DAting System) accelerator system[21]. The samples were analysed with an elemental analyser coupled to the MICADAS via a gas interface. Details of the method are given elsewhere[22–24]. Briefly, liquid samples (10 µL containing 20 µg ^{12}C) or standards crystals, containing ~50 µg ^{12}C, were packed in tin capsules or foil, respectively, to allow for flash combustion. The samples were loaded into the autosampler of the elemental analyser (EA, Vario Micro Cube, ELEMENTAR, Hanau, Germany) which injected them into an oven at 850 °C for combustion with a pulse of oxygen. The EA directs the gases through a water trap containing Sicapent (Merck, Germany) and through a zeolite trap which was subsequently heated up stepwise to consecutively release N_2, CO_2 and residual gases. The outlet of the EA was connected to a gas interface system (GIS) through a 1/16'' O.D. tubing (10 m long). CO_2/He mixtures were directed to a second zeolite trap (zeolite X13, Sigma–Aldrich, Germany) installed in the GIS at a flow rate of 80 mL/min regulated by a mass flow controller located at the GIS entrance. The GIS and the trap are described in detail elsewhere[25].

The GIS trap was heated up to 450 °C, thus allowing the CO_2 to desorb and expand into a syringe of known volume which plunger was controlled by a stepper motor. The carbon content was manometrically determined. Helium was added to prepare a mixture of 5% CO_2 at ~ 0.16 MPa. Eventually, the mix was transferred into the gas ion source of the MICADAS AMS at ~ 40 µL/min. Simultaneously with the measurement, a flushing step was applied to the EA-GIS system for 4 min which consisted on running the EA at 100 mL/min without adding a sample, and heating up the CO_2 trap of the EA. This high flow was directed to the GIS trap which, at the same time, was heated up for flushing. The entire procedure was automatically controlled by a LabView program based on an earlier version reported in Wacker et al.[25].

The standards used to calibrate the AMS were crystals of sodium acetate (fossil; p.a., Merck, Germany), C5, C6 and C7 from IAEA[26] and oxalic acid II from NIST (SRM 4990C) with nominal ^{14}C contents of 0.2305 ± 0.0002 $F^{14}C$, 1.5061 ± 0.0011, 0.4935 ± 0.0012 $F^{14}C$ and 1.3407 ± 0.0005 $F^{14}C$, respectively.

AMS measurements and data presentation

In AMS measurements, $^{14}C/^{12}C$ ratios are determined. Since the samples obtained from the ion-exchange chromatography contain very little carbon (a few ng), it is necessary to add a defined quantity of ^{14}C-free (fossil) carbon carrier in order to reach the stable carbon content required for AMS. . For this purpose, a sodium acetate solution (30 µg ^{12}C/µL) was prepared to spike the samples with ^{12}C, thus yielding a final concentration of 2 µg ^{12}C/µL in the samples. After addition of the ^{12}C carrier, the samples were

immediately frozen to -20 °C and stored at this temperature until the AMS analysis was performed.

The $^{14}C/^{12}C$ ratio determined by AMS is expressed in terms of fraction of modern carbon ($F^{14}C$). This latter unit can be related to the concentrations of ^{14}C of the various organic molecules in the leaching solution (mol ^{14}C/L) by considering that 2 µg ^{12}C/µL of carbon and 10 µL per injection of leaching solution were injected into the AMS. Taking the experimental parameters into account a conversion between the units can be applied[27]:

$$1\ F^{14}C \equiv 2.74 \cdot 10^{-12}\ g\ ^{14}C/L = 195.7\ fmol\ ^{14}C/L = 0.452\ Bq/L \quad (1)$$

Blank samples were prepared from the ^{14}C-free sodium acetate solution (2 µg ^{12}C/µL). The blanks were run to identify possible contaminations and were subjected to the same treatments as the samples. Furthermore, blank samples were run during the HPIEC analysis and prepared for each set of injections. The blank samples were either prepared in ultrapure water or ACW solution that had been passed through the OnGuard® cartridge. The blanks were treated and injected in the same conditions as the subsequent samples prepared for the AMS analysis and were subjected to collection of fractions at the retention time of the targeted fractions and analysed by AMS along with these fractions.

Results and discussion

Development of chromatographic fractionation by HPIEC

The analytical approach for the compound-specific AMS-based detection of ^{14}C-bearing organic compounds is schematically shown in Fig. 1. In this approach HPIEC allows the separation of carboxylic acids that are expected to be released during iron corrosion[8]. Analytical separation was optimized for the main target carboxylic acids, that is formic acid (FA), acetic acid (AA), oxalic acid (OA) and malonic acid (MA), and recovery and repeatability were checked. For this purpose, a mixture with known concentrations of the four fossil carboxylic acids (500 µM for AA and FA, 200 µM for OA and MA) was injected and fractions were collected. The concentration of each fraction was quantified using conductivity detection and compared with the initial concentration of the mixture to calculate the recovery. Recovery was determined from triplicates as follows: AA = 100 ± 7 %, FA = 95 ± 6 %, MA = 99 ± 3 %, OA = 96 ± 4 %. This shows a high recovery rate and repeatability of the fractionation process.

Determination of the ^{14}C background

The concentrations of the carboxylic acids released during the corrosion of irradiated steel were expected to be at the ultra-trace level, resulting in femto- to picomolar solutions of ^{14}C. Therefore, contamination by naturally occurring ^{14}C in air could not be ignored.

Primarily the potential ingress of modern $^{14}CO_2$, especially into alkaline solutions, has to be eliminated. Thus, atmospheric ^{14}C along with additional potential sources of background ^{14}C during analysis were identified and assessed experimentally, which includes: glass/plastic containers and vials used to store the solutions, residual chromatographic eluent and column bleeding, atmospheric leaks during transport of the frozen samples to the AMS facility and eventually the AMS measurement. The detection limit is considered to be determined by the method-induced background, potentially determined by the aforementioned various steps in the course of sample preparation, handling and measurement.

A cleaning procedure for the sample vials was applied to minimize the background. All vials were pre-cleaned by repeatedly rinsing with ultrapure water. To this end, the vials were soaked in ultrapure water in a closed container for a period of at least 7 days while the water was replaced daily. Eventually, the vials were stored in ultrapure water and dried with nitrogen prior to use. The effect of the cleaning procedure and sample treatment on the background was tested for sample vials fabricated from different materials, e.g. polypropylene (PP) and glass, and using water with different levels of purity, e.g. deionized water, ultrapure water and boiled ultrapure water (Table 1).

No significant difference in the ^{14}C background for the pre-cleaned plastic and glass vials was observed. A background of about 11 ± 4 fmol ^{14}C/L (0.06 ± 0.02 $F^{14}C$) or 12 ± 4 fmol ^{14}C/L (0.06 ± 0.02 $F^{14}C$) was determined for the different vials. In addition, untreated ultrapure water did not show a higher background compared to ultrapure or degassed ultrapure water. Also, ultrapure water and ACW run through the system and collected at the retention times of the four carboxylic acids did not show an increased background. However, a significant increase in the fraction modern carbon was observed for an ACW-solution (stored under nitrogen atmosphere for a few weeks) which was not subjected to pre-treatment by passing through the cartridge (123 ± 67 fmol ^{14}C/L; 0.63 ± 0.34 $F^{14}C$). This increase in the ^{14}C background is most likely caused by the ingress of atmospheric CO_2, which contains a contemporary concentration of $^{14}CO_2$, into the alkaline solution during sample preparation, transportation and the AMS measurement. This finding shows that alkaline solutions should either be handled in a controlled $^{14}CO_2$-free atmosphere or neutralized immediately after sampling to avoid ingress of $^{14}CO_2$ from the laboratory environment.

Table 1 ^{14}C background.

Vial [fmol ^{14}C/L]		Solvent[1] [fmol ^{14}C/L]		IC-fraction [fmol ^{14}C/L]			
PP	11 ± 4	Ultrapure water	11 ± 4	Ultrapure water-AA	13 ± 5	ACW-AA	12 ± 4
Glass	12 ± 4	Deionized water	13 ± 4	Ultrapure water-FA	8 ± 7	ACW-FA	10 ± 5
		Boiled ultrapure water	21 ± 13	Ultrapure water-MA	5 ± 3	ACW-MA	12 ± 5
		ACW (pH 12.5)	123 ± 67	Ultrapure water-OA	4 ± 3	ACW-OA	11 ± 3

[1] tests performed using pre-cleaned polypropylene (PP) vials

In subsequent tests, the effect of fractionation on the ^{14}C background was determined. To this end, ultrapure water was injected into the IC and fractions were collected at the retention times corresponding to those of the four carboxylic acids. It was acknowledged that various materials (e.g. analytical column, eluent and laboratory atmosphere) could interact with the sample during fractionation which could result in an enhanced ^{14}C background. Note that the collected fractions were neutralized to a pH between 6 and 7 in the ion suppression unit of the IC during fractionation. In addition, all samples prepared for the AMS measurements were frozen to -20 °C instantaneously after fractionation to avoid ^{14}C ingress and (microbial) degradation of the analytes.

The ^{14}C background determined after fractionation of acetic acid, formic acid, malonic acid and oxalic acid ranged between 4 and 13 fmol ^{14}C/L (0.02 - 0.06 F^{14}C) which is comparable to the background when the samples were just dissolved in ultrapure water without performing chromatography. Hence, an enhancement in the background was not observed in the course of the fractionation process. This finding clearly shows that, given that no alkaline solution was involved, the compound-specific AMS-based analytical method allows very low ^{14}C concentrations to be determined as no major ^{14}C contamination occurs. To summarize, an average ^{14}C background of 11 ± 4 fmol ^{14}C/L (0.06 ± 0.02 F^{14}C) was determined in the samples after fractionation using pre-cleaned PP vials for injection and collection. Taking the average of the blank measurements (a_{blank}) and the standard deviation of the blank measurements (s_{blank}) into account the limit of detection (LOD) can be calculated as follows:

$$LOD = a_{blank} + 3 \cdot s_{blank} \quad (2)$$

For our experimental approach this results in a LOD of 23 fmol ^{14}C/L or 0.12 F^{14}C.

Recovery tests with single compounds in ultrapure water and determination of the dynamic range of the method

^{14}C-labelled carboxylic acids (^{14}C-AA, ^{14}C-FA, ^{14}C-MA, ^{14}C-OA) were used for the recovery tests aimed at determining the dynamic range of the AMS system and the individual recovery rates during fractionation. The results obtained with ^{14}C-labelled acetate (^{14}C-AA) are exemplarily listed in Table 2. Solutions with different molar concentrations of the individual ^{14}C-labelled carboxylic acids, corresponding to 1.9 - 494 pmol ^{14}C/L (9.7 – 2527 F^{14}C; in a matrix of 20 µg ^{12}C per injection), were prepared and injected into the IC system (Fig. 1). The fractions of the carboxylic acids were collected and analysed by AMS. The expected ^{14}C-AA concentration and fraction modern carbon in the collected fraction should correspond to 41 - 9881 fmol ^{14}C/L (0.22 – 50.5 F^{14}C; in a matrix of 20 µg ^{12}C) due to a 1:50 dilution during the IC injection/collection steps. Table 2 shows the expected activity, the concentration measured with AMS and the recovery estimated as the ratio of the two values (in %). The average recovery determined from the samples in the concentration range between 104 - 9881 fmol ^{14}C/L (0.5 – 50.5 F^{14}C) was close to 100 % (96 ± 7 %). Note, however, the rather poor recovery observed at the lowest concentration (39 fmol ^{14}C/L, 0.21 F^{14}C) which was close to the LOD of the method (23 fmol ^{14}C/L, 0.12 F^{14}C). This is also depicted by the low precision of the measurement at this concentration. Overall, the results indicate complete recovery of ^{14}C-labelled acetate after fractionation.

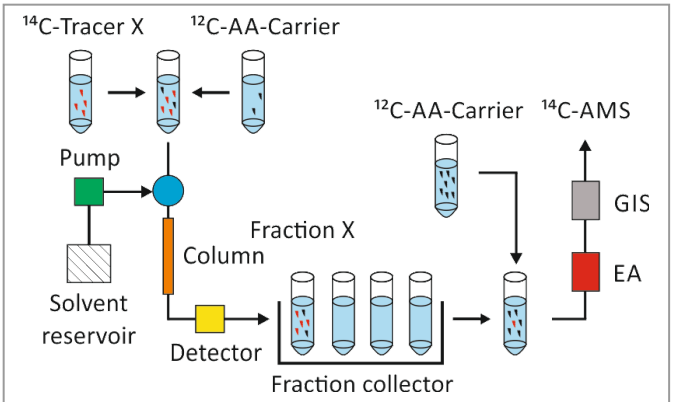

Fig. 1 Scheme of the experimental setup used for the recovery test of a carboxylic acid X.

In addition, these experiments enabled us to determine the linear dynamic range of the AMS. The maximum applicable ^{14}C concentration was determined to be 14.8 pmol ^{14}C/L (75 F^{14}C). However, undesirable memory effects were observed at such high ^{14}C concentrations which prompted us to limit the maximum concentration at 9.8 pmol ^{14}C/L (50 F^{14}C). Hence, the linear dynamic range extends over three orders of magnitude, i.e. from 0.01 to 9.8 pmol ^{14}C/L (0.06 to 50 F^{14}C). This wide dynamic range provides the required flexibility of measuring low and concentrated samples without re-adjusting the method.

Table 2 Recovery of ^{14}C-labelled acetate after IC fractionation and analysis using AMS.

Expected [F^{14}C]	Expected [fmol/L]	Measured [fmol/L]	Recovery [%]
0.21	39	26 ± 9	67 ± 23
0.53	104	103 ± 13	99 ± 12
1.06	207	191 ± 17	92 ± 8
3.00	586	572 ± 36	98 ± 6
4.95	968	1011 ± 58	104 ± 6
11.73	2296	2220 ± 119	97 ± 5
25.30	4951	4562 ± 236	92 ± 5
50.50	9881	8965 ± 456	91 ± 5

Recovery of single ^{14}C-bearing carboxylic acids and mixtures in ACW solution

Recovery tests with the four different ^{14}C-labelled carboxylic acids (^{14}C-AA, ^{14}C-FA, ^{14}C-MA and ^{14}C-OA) were performed in ACW. The samples were subjected to cartridge treatment and subsequently injected into the IC system as single compounds. The corresponding fractions were collected and analysed by ^{14}C AMS. Along with the collected fractions also the starting solutions were analysed to enable a direct comparison of the concentrations before and after fractionation. The concentration of the injected starting solution was 9.8 pmol ^{14}C/L (50 F^{14}C) for ^{14}C-AA, ^{14}C-FA, ^{14}C-MA and ^{14}C-OA. Recoveries (%) were estimated by considering the dilution factor during fractionation for each compound. Recoveries of the single compounds were determined to be ^{14}C-AA = 104 ± 6 %, ^{14}C-FA = 96 ± 4 %, ^{14}C-MA = 52 ± 10 % and ^{14}C-OA = 52 ± 5 %. The results show full recovery in case of ^{14}C-labelled formate and acetate, while only ~50% recovery was achieved in case of oxalate and malonate. The latter observation was found to be reproducible throughout the experiments, but the reason remains unclear. To account for the low recovery of malonate and oxalate fractions, the data of the following leaching experiment was corrected by assuming only 50% recovery for these two substances.

After verifying the repeatability of the method for the single compounds, a mixture of ^{14}C-AA, ^{14}C-FA, ^{14}C-MA and ^{14}C-OA with activities corresponding to 4.7, 4.7, 2.3, 2.3 pmol ^{14}C/L (23.8, 23.8, 11.7, 11.7 F^{14}C), respectively, were prepared in ACW solution. Samples were pre-treated, separated and analysed as described in the previous section.

The ^{14}C concentration of the starting mixture used for fractionation was also determined by AMS. After injecting an aliquot of the mixture the remaining solution was weighed and ^{14}C-free acetate carrier was added to achieve a total ^{12}C content of 2 µg/µL. The recoveries for the single fractions determined from the mixture containing all ^{14}C-labelled carboxylic acids were as follows: ^{14}C-AA = 101 ± 4, ^{14}C-FA = 96 ± 3, ^{14}C-MA = 59 ± 5

and ^{14}C-OA = 68 ± 5. The lower recoveries for malonic and oxalic acid in this experiment correspond to those observed for the analysis of the single compounds.

Cross contaminations

The possibility of cross contaminations was checked for both IC fractionation and ^{14}C detection by AMS.

IC measurements. Cross contamination was determined from alternating injections of ultrapure water and samples of ^{14}C-labelled carboxylic acid with the highest ^{14}C concentration (corresponding to 2500 F^{14}C in a matrix of 20 µg ^{12}C). The eluate was collected according to the retention times of the carboxylic acids of interest. The tests showed that the ^{14}C background was not enhanced after injecting the highly concentrated ^{14}C standards. This indicates that cross contamination was below the detection limit during fractionation.

IC-EA-AMS measurements. Cross contamination often occurs in the elemental analyser and the GIS, when samples with a wide range of concentrations are measured. If the concentration (R_x) and mass (m_x) of the previous active samples are high enough, it is possible that a small fraction (φ) remains inside of the measuring instrument, mixing with the mass (m_s) and concentration (R_s) of the next sample. The mixing will lead to an incorrect measured concentration (R_m). Note that cross contamination is considered to be constant for the analysis of ^{14}C/^{12}C. Therefore, it is possible to subtract and correct the contamination from the measured value. A ^{14}C mass balance analysis of cross contamination is given by[22]:

$$R_m - R_s = \frac{\varphi m_x}{m_s}\left(R_x - R_s\right) \qquad (3)$$

The experiment to check cross contamination consisted of alternating injections of ^{14}C-labelled acetic acid (R_x) and ^{14}C-depleted sodium acetate (R_s = 0 F^{14}C) into the IC, collect and analyse the eluate with the AMS coupled to the EA and GIS. The sample mass for both substances was kept constant ($m_s = m_x$ = 20 µg). Fig. 2a shows the plot of R_m vs R_x. The slope corresponds to the cross contamination factor φ = 0.45 %. Fig. 2b further shows the ^{14}C/^{12}C ratios given in Fig. 2a corrected with equation 4:

$$R_{corr} = \left(\frac{m_s R_m - \varphi m_x (R_x - R_0)}{m_s - \varphi m_x}\right) \qquad (4)$$

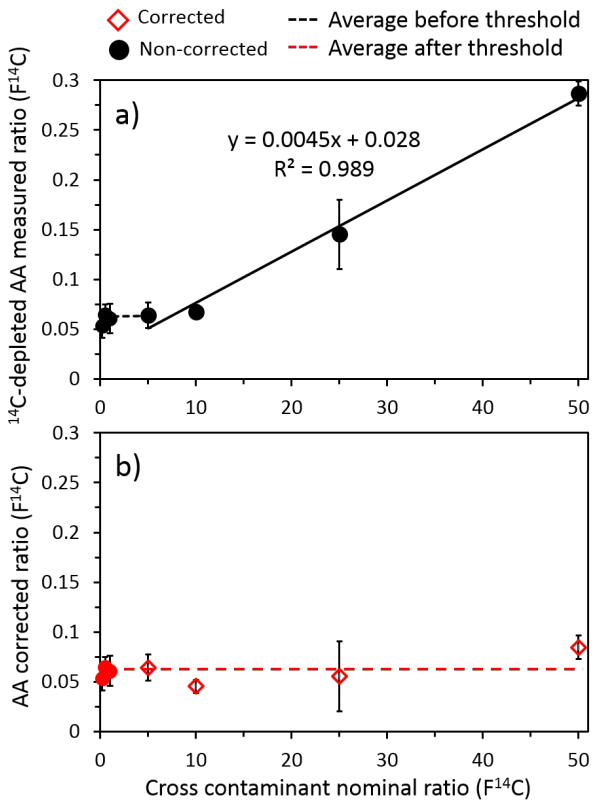

Fig. 2 a) Cross contamination for the entire IC-EA-AMS system. Samples were injected into the IC and analyzed with the EA-AMS system. a) Measured $F^{14}C$ of acetic acid depleted in ^{14}C which was cross contaminated with a previous injection of acetic acid with a high $^{14}C/^{12}C$ ratio ("hot sample"). Closed circles indicate the region where the cross contamination model behaves linearly. b) Same data as (a) but the cross contamination was linearly corrected using eq. 4 for "hot samples" R_x values are equal or higher than the threshold (R_0 = 5 $F^{14}C$). Closed circles indicate the start of the region where cross contamination is small which extends until the beginning of the linear region indicated by a dashed line.

A comparison of the previously determined background level (0.06 ± 0.02 $F^{14}C$) with the data displayed in Fig. 2b shows clearly how the contaminated values of the ^{14}C-depleted substance return to background levels. These results support the fitting and correction of the cross contamination based on Eqs. 3 and 4. Especially for high ^{14}C activities, cross contamination might affect the obtained results. Therefore this effect was accounted for in the data treatment for all samples.

Analysis of the leachate of an irradiated steel nut specimen

The CSRA AMS-based analytical method was developed with the aim to determine the concentration of ^{14}C-bearing carboxylates in alkaline solution from a leaching experiment with irradiated steel and in a corrosion experiment with irradiated steel in anoxic

conditions[28]. The concentrations of the ^{14}C-bearing compounds were expected to be extremely low (femto to pico molar). Due to radiation protection only a small amount of irradiated steel could be used in the leaching experiment and the low ^{14}C inventory along with the very slow corrosion of steel in alkaline solutions led to the very low ^{14}C concentrations. Corrosion occurring at the surface of irradiated steel and the release of ^{14}C-bearing organic compounds from the oxide layer of the corroding steel are expected to be the two chemical reactions that produce the aqueous ^{14}C-bearing species in the leaching experiments.[8] Analysis of the leaching solution enabled us to prove whether or not the CSRA AMS-based analytical method was suited to identity and quantify ^{14}C-bearing carboxylic acids.

^{60}Co release. The experimentally determined ^{60}Co activity in solution can be compared with the modelled ^{60}Co release from the steel specimen during leaching (Fig. 3). Modelling was based on the known surface area of the steel segment and the measured ^{60}Co inventory (^{60}Co: 61.7 ± 2.2 MBq/g)[13]. Furthermore, it was assumed that ^{60}Co was only released by corrosion and the corrosion rate was adjusted to fit the experimental data. The best fit to the data was achieved by modelling a fast initial release of ^{60}Co (~100 nm/a) followed by decelerated corrosion (~3 nm/a) after ~10 days. This implies that fast corrosion only occurs over a limited period of time, probably due to the presence of residual O_2 in solution or the presence of very reactive surface sites of the irradiated steel segment. At the later stage, however, the corrosion rate is much smaller in accordance with an anoxic corrosion process. Note that re-absorption of ^{60}Co by the surface layer of steel could have an effect on the apparent corrosion rate. This process would result in underestimating the amount of ^{60}Co released during corrosion (absolute level) while it would not change the overall picture of the temporal evolution of the corrosion process.

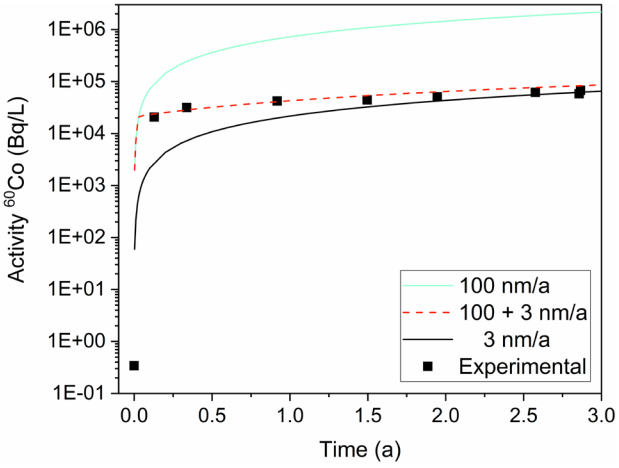

Fig. 3 Activity of ^{60}Co released during corrosion of activated steel. Comparison of experimental results with simulated activities derived from various corrosion rates[13].

Quantification of ^{14}C-bearing organic compounds. An aliquot from the leachate was withdrawn after 1046 days reaction time and, after the cartridge treatment, analysed using the previously described CSRA AMS-based analytical method for carboxylates. The

results are presented as measured concentration in the fractions and as dilution-corrected concentration of the initial sample solution before fractionation (Table 3). They show that the concentrations of the ^{14}C-bearing carboxylates are well above the detection limit of the method (23 fmol) except for malonic acid. The concentration of the individual compounds in the fractions collected after fractionation ranged between 87 – 216 fmol ^{14}C/L or 30 – 200 µBq/fraction, respectively. Nevertheless, this concentration level is far below the LOD of liquid scintillation counting (LSC), which is the standard laboratory technique used for ^{14}C anaylsis (LOD of LSC: ranging from 10.000 µBq (best measuring conditions) to 80.000 µBq (standard conditions)). Thus, between 50 and 330 fractions produced by IC would be required in order to be able to determine the ^{14}C activity of the individual compound above the LOD of LSC. Notably, collection of so many fractions would take between 2 and 14 days only for sample fractionation and eventually it would make it very difficult to use LSC for ^{14}C detection due to the large sample volume (25 - 80 mL). Our measurements clearly demonstrate the possibility to identify and quantify ^{14}C-bearing compounds in the femto - to pico molar concentration range using AMS.

Table 3 Concentrations of the collected fractions with and without dilution correction.

Sample	Measured concentration		Corrected concentration
	$F^{14}C$	pmol/L	pmol/L
AA - fraction	**0.89 ± 0.31**	**0.17 ± 0.06**	**6.20 ± 2.14**
FA - fraction	**0.59 ± 0.23**	**0.12 ± 0.05**	**4.09 ± 1.62**
MA - fraction	**0.34 ± 0.23**	**0.07 ± 0.05**	**2.36 ± 1.62**
OA - fraction	**0.32 ± 0.11**	**0.06 ± 0.02**	**2.21 ± 0.76**
Sum:	-	-	**14.87 ± 6.14**

The results show that ^{14}C-bearing acetate and formate are the main carboxylates formed during leaching of the irradiated steel nut specimen. It should be noted that carboxylates had previously been identified as important products in alkaline solution formed during the anoxic corrosion of non-irradiated iron powders[8]. Therefore, this study shows that carboxylic acids are also formed during leaching of irradiated steel.

Total organic ^{14}C content (TO^{14}C) in solution. The TO^{14}C accounts for the total concentration of ^{14}C dissolved in the organic chemical form in solution. The presence of ^{14}C in the inorganic chemical form, i.e. $^{14}CO_3^{2-}$, in strongly alkaline solutions can be excluded in this study because of the cartridge pre-treatment which reduced pH to near-neutral values by Ca-H exchange. Test experiments using ^{14}C-labelled carbonate showed that due to this change in pH during the pre-treatment more than 97% of the inorganic carbon was removed from the sample solution.

In this study, the TO^{14}C was determined in two different ways, 1) by the determination of the concentration of the individual ^{14}C-bearing carboxylates (see previous section) and 2) by direct determination of TO^{14}C in an aliquot of the leaching solution.

The total organic ^{14}C (TO^{14}C) content based on the analysis of the individual ^{14}C-bearing carboxylic acids was determined to be 14.9 ± 6.1 pmol/L ^{14}C (76.2 ± 31.2 F^{14}C) (Table 3). The direct measurement resulted in a TO^{14}C of 8.9 ± 1.8 pmol/L ^{14}C (45.5 ± 9.2 F^{14}C). Thus, the TO^{14}C content determined by the two analytical approaches are consistent within the uncertainties, which also implies that the investigated ^{14}C-bearing carboxylates are the major fraction of the TO^{14}C content.

The temporal evolution of TO^{14}C in the leaching experiment was modelled based on the following input data and assumptions: 1) surface of the 1 g specimen (6.49 cm^2/g) and ^{14}C inventory of irradiated steel (17.8 ± 2.5 kBq/g corresponding to 0.107 ± 0.015 µg ^{14}C/g or 7.71 ± 1.08 nmol ^{14}C/g)[13], 2) initial volume of the alkaline solution (29.3 mL), 3) corrosion rates determined from ^{60}Co release (initial phase: 30 days at 100 nm/a; steady state: 3 nm/a as shown in Fig.3), 4) only the organic chemical form of ^{14}C species (i.e. carboxylates) was produced during corrosion. Changes in the TO^{14}C with time as shown in Fig. 4 were modelled for corrosion rates of 3 and 100 nm/a over the entire period of the experiment as well as by considering decelerated corrosion with time, i.e. 100 nm/a in the initial phase and 3 nm/a at steady state, as evidenced from ^{60}Co release. The modelled data can be compared with the experimental ones, i.e. the TO^{14}C content determined by direct measurement and as a sum of the individual fractions. Modelled and experimental data agree very well. This indicates that ^{14}C released from irradiated steel was predominantly converted into dissolved ^{14}C-bearing organic compounds i.e. TO^{14}C). Note, however, that a critical appraisal of this conclusion would require the possibility of the formation of volatile species in the system to be checked. Nevertheless, in this experiment the set-up was not designed in such a manner to allow gas phase analysis.

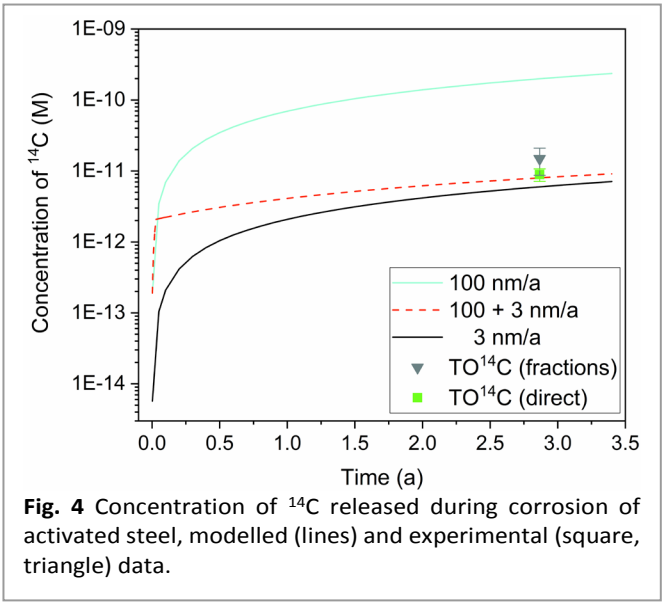

Fig. 4 Concentration of ^{14}C released during corrosion of activated steel, modelled (lines) and experimental (square, triangle) data.

Conclusions

A CSRA AMS based method was successfully developed which allows extremely low concentrations of ^{14}C-bearing carboxylic acids to be detected (femto - to pico molar concentration) in alkaline solutions. The method was applied to a leaching experiment with irradiated steel with the aim to determine ^{14}C-bearing organic compounds released during corrosion in alkaline media. ^{14}C-bearing formate and acetate were the main organic corrosion products while ^{14}C-bearing malonate and oxalate were present at lower concentration. Formate and acetate have previously been identified as important organic corrosion products in non-irradiated iron-water-sytems[8]. The CSRA AMS method will be employed in a well-controlled corrosion study with irradiated steel conducted in O_2-free conditions allowing also gas phase analysis[28]. Information on the chemical nature of the ^{14}C-bearing compounds produced during the corrosion of irradiated steel in alkaline solution will support safety assessments performed for the long-term safe disposal of radioactive waste containing irradiated metallic materials.

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